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"**Enhancement of grain refined microstructurein a nanostructured metals via ultrahigh pressure hydrostatic consolidation process**

- Construction of Master Sintering Curve (MSC) and its application to densification of Al-Mg alloy"

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Abstract: Previously Al-Mg alloy was densified by hot isostatic processing and subsequently consolidated by hydrostatic extrusion. Through this process high strength and high formability nanostructured bulk Al-Mg alloy was fabricated. However, it is important to handle parametric control in powder metallurgical processing in terms of relative density, which is closely associated with its mechanical properties in acquiring a material of a desired property. At current stage processing parameter of density function is not controllable. In this study a concept of Master Sintering Curve (MSC) theory was introduced and applied to the examined material during densification to obtain a unified MSC allowing for predicting density variation in terms of only sintering time and temperature in regardless of thermal history at certain compaction pressure. After completing MSC new experimental set of time-temperature data were fitted to validate the derived MSC curve in such a way that it is completely coincident with new set of experimental data in tolerable error. Hardness measurement was conducted to study the effect of heating rates.

Introduction: A sequence of several powder metallurgical processing was developed earlier to fabricate nanostructured Al-Mg alloy with high strength and high formability. The process has 3 stages. First, cryogenic milling process – powder milling in liquid N_2 at cryogenic temperature- is to mill metallic powders with a few tens to a few hundreds of grain size to reduce to a few tens of nanometer grains. Second, cryomilled powders are consolidated by Hot Isostatic Pressing (HIP) or unidirectional hot pressing to make a sintered compact. It is, third, subsequently extruded hydrostatically to obtain high toughness bulk nanostructured alloy, which was successful up to this point. However, in the metallurgical engineering point of view, it is required to have tailored nano-structured materials with desirable properties. In order to do that it is necessary to control processing parameters to manipulate internal structures such as density, microstructure or grain size etc. For instance, a major issue in dealing with powder sintering is how to achieve fully dense state in the material with minimization of microstructural coarsening and undesirable microstructural transformation and how to consolidate the particles at lower temperature in shorter time etc. In order to do it, it is inevitable to associate external parameters such as pressure, temp, time to internal variation like density change and/or grain growth. As a fundamental research step to explore a relation among these parameters, a very useful theory called Master Sintering Curve (MSC) Theory is introduced in this study. Although this theory is applied to the consolidation of Al-4%Mg alloy only by unidirectional hot pressing, theory would be definitely extended to Hot Isostatic Pressing (HIP) and Hydrostatic Extrusion (HE) provided real-time bulk shrinkage measurement is precisely possible.

Hot pressing is an effective method for densification of material using thermal and mechanical energy. It can fabricate fully dense, fine-grained ceramic bodies at lower temperatures and at a shorter cycle times than those required by conventional sintering. Among several mechanisms proposed to explain the observed enhanced densification during hot pressing, Master Sintering Curve (MSC) theory developed (limited only to pressureless sintering) by Su and Johnson for pressureless sintering would be utilized here.

The MSC characterizes the sintering behavior for given powders regardless of the heating history. The MSC was derived from a combined stage sintering model which includes both volume and grain-

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14. ABSTRACT
Previously Al-Mg alloy was densified by hot isostatic processing and subsequently consolidated by hydrostatic extrusion. Through this process high strength and high formability nanostructured bulk Al-Mg alloy was fabricated. However, it is important to handle parametric control in powder metallurgical processing in terms of relative density, which is closely associated with its mechanical properties in acquiring a material of a desired property. At current stage processing parameter of density function is not controllable. In this study a concept of Master Sintering Curve (MSC) theory was introduced and applied to the examined material during densification to obtain a unified MSC allowing for predicting density variation in terms of only sintering time and temperature in regardless of thermal history at certain compaction pressure. After completing MSC new experimental set of time-temperature data were fitted to validate the derived MSC curve in such a way that it is completely coincident with new set of experimental data in tolerable error. Hardness measurement was conducted to study the effect of heating rates.

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boundary diffusion mechanisms. The instantaneous densification rate in this model is

$$-\frac{d\rho}{\rho dt}=\frac{\gamma\Omega}{kT}\left(\frac{\Gamma_V D_V}{G^3}+\frac{\Gamma_b \delta D_b}{G^4}\right) \quad (1)$$

Where γ is surface energy, Ω the atomic volume, k the Boltzman constant, T absolute temperature, G the grain diameter, D_V and D_b the coefficients of volume and grain boundary diffusion, respectively and δ the width of the grain boundary. D_V and D_b (non-constant) lumped scaling parameters that relate various geometric features, the driving force for sintering, and the mean diffusion distance to the grain size.

This equation can be rearranged for either grain boundary or volume diffusion such that all terms that are not explicitly functions of temperature are carried to left hand side, then integrated as follows:

$$\frac{k}{\gamma\Omega D_0}\int_{\rho_0}^{\rho}\frac{(G(\rho))^n}{3\rho\Gamma(\rho)}d\rho=\int_0^t\frac{1}{T}\exp\left(-\frac{Q}{RT}\right)dt \quad (2)$$

Where Q is the apparent activation energy, D_0 is the pre-exponential term for the diffusion coefficient, R is the gas constant, and n=3 or 4 for volume or grain boundary diffusion, respectively. A mechanistic model would attempt to integrate both sides of this equation. For the master sintering curve, the measured density can be predicted from the curve irrespective of the heating path.

The motivation of present study is to determine whether the concept of the master sintering curve can be extended to the realm of hot pressing, and to establish the "pressure-assisted" master sintering curve of Al-Mg alloy, and if successful, it would be further extended to HIP and HE to control the density and internal structural variation. In this respect exploration of MSC in hot pressing would be the very fundamental research for fabrication of powder metallurgical material to give tailored solution to obtaining desired properties.

Experiment: Pure Aluminum and pure magnesium were alloyed by spray drying process with proper weight fraction to produce Al-4%Mg alloy powders. Table 1 shows the chemical composition of the Al-4%Mg alloy.

Table 1 chemical Composition of Al-4%Mg alloy

Alloy	Mg	Mn	Zn	Si	Cu	Ni	Fe	Al
Al-4%Mg	4.0	0.59	0.03	0.15	0.39	0.02	0.24	Bal.

The acquired particles were screened and ones with the size less than 45μm were collected and preserved in Argon atmosphere in a glove box to minimize further oxidation at the surface of the powder for future use. Fig. 1 shows the SEM microphotograph of Al-4%Mg alloy powders.

Densification was conducted under a constant pressure of 20 and 50 MPa at elevated temperatures in Hot Pressing Machine shown in Fig. 2. Initially, the powders were roughly compacted in a hollow graphite mold and the mold was properly located in the pressing chamber and a plunger at top of the chamber was pull down onto the top surface of the powders to exert a constant pressure. After locking up the chamber, the temperature was ramped up to two different peak temperatures. First, temperature was raised up to 400 ℃ and stayed with 30 min holding time. Second, temperature was raised up to 500℃ without holding time.

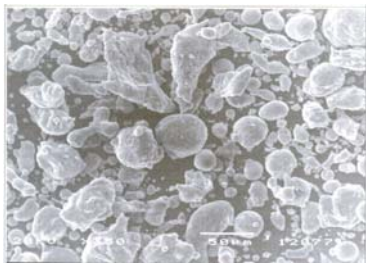


Fig. 1 SEM image of Al-4%Mg alloy powders

Fig. 2 Hot Press Machine

Experiments were performed at 3 different heating rates of 5, 10 and 20℃/min. Vacuum was maintained at 10^{-5} torr during densification process by sintering mechanism. As soon as densification was complete, the specimen was cooled down to room temperature in the furnace. Experimental schedules of densification at elevated temperatures are shown in Table 2.

Table 2 Experimental schedule for the densification of Al-4%Mg alloy powders

(a) 1st schedule

Temperature (℃)	400					
Holding time (min)	30					
Pressure(MPa)	20			50		
Heating rate(℃/min)	5	10	20	5	10	20

(b) 2nd schedule

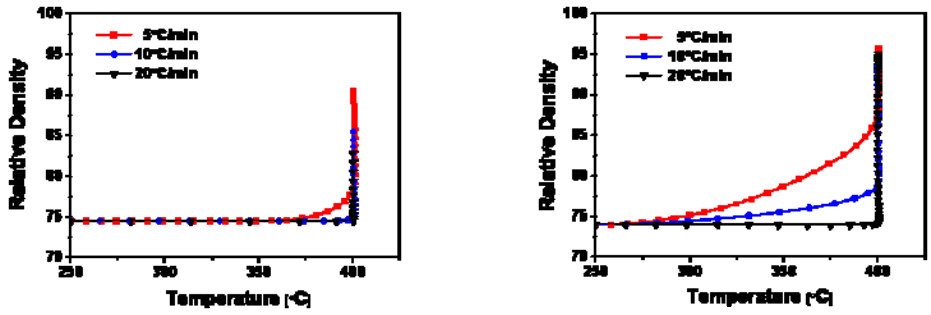
Temperature (℃)	500					
Holding time (min)	N/A					
Pressure(MPa)	20			50		
Heating rate(℃/min)	5	10	20	5	10	20

During the experiment the length change measurement of Al-4%Mg alloy was carried out by a linear voltage differential transducer (LVDT). The temperature was measured by a C-type thermocouple at the nearest proximity of the specimen. During the specimen was heated, its temperature and length values were measured continuously using a thermocouple and LVDT, respectively. The shrinkages were recorded automatically by a computer. The sintered density was measured by geometric method. Vickers hardness was measured and compared for each specimen before and after densification.

Results and Discussion:

1. MSC Construction

For the construction of MSC, the intergral of Eq. (1) and the experimental density should be known. Fig. 3 shows the time-dependent relative density versus temperature converted from dilatometer data. For the calculation of $\Theta(t, T(t))$, the activation energy must be known. If the activation energy is unknown, it can be estimated with good precision from Θ versus density (ρ) data. The apparent activation energys for the MSC of densification are determined by minimizing mean residual method.



(a) (b)

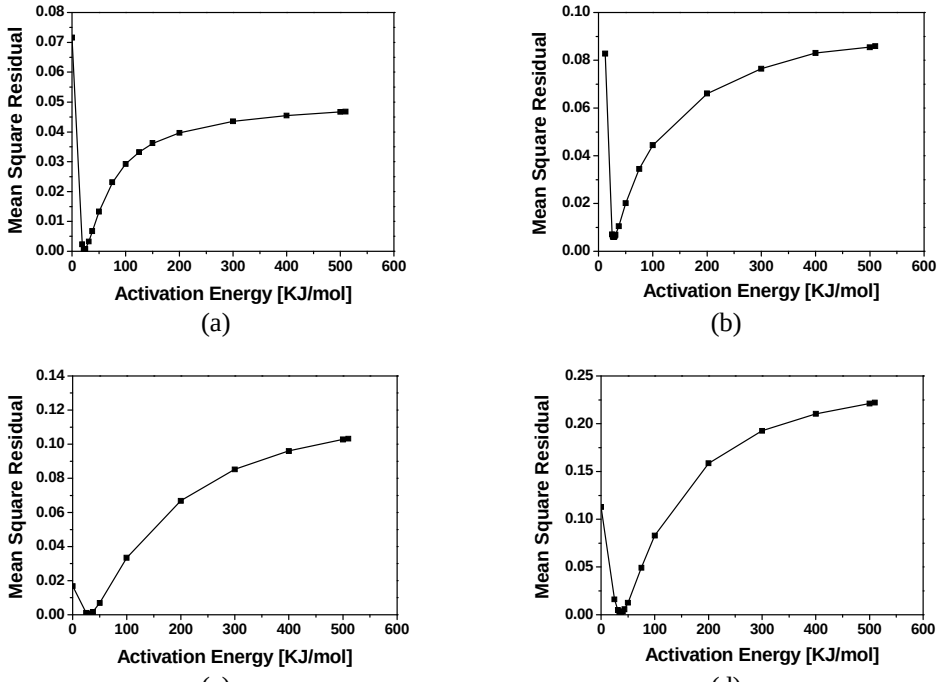
Fig. 3 The plot time-dependent relative density vs. temperature at (a) 20MPa, and (b) 50MPa

For this purpose initially, an estimate is made for the activation energy *Q*, and the MSCs for three heating profiles are computed using Eq. (1). If the correct value of Q has been given, all of the data converge to a single curve. A curve can be fitted to all the data points, and the convergence of the data to the fitted line can be quantified through the sum of the residual squares of the points with respect to the fitted line. Another estimate of Q is made, and the process is repeated. When the best estimate of Q is found, the mean residual is a minimum. By applying this process to the data acquired from 1st and 2nd schedules, the activation energies were obtained as following:

Table 3 The Activation energy Q calculated from the mean residual method

Schedule	Peak at 400℃ with 30 min holding		Peak at 500℃ with no holding	
Pressure (MPa)	20	50	20	50
Q (kJ/mol)	23.1	28	29.6	36.4

As seen in the Table 3, the estimated activation energies of densification or sintering range from 23.1 to 36.4 kJ/mol. Fig. 4 shows the minimum of mean square residual in terms of activation energy for each thermal history.



(a) (b)

(c) (d)

Fig. 5 The activation energy obtained by MSR Method (a) under 20 MPa and (b) 50 MPa for Schedule1 and (c) under 20 MPa and (d) 50 MPa

From the knowledge of activation energies of sintering above, master sintering curves were obtained in each case, shown in Fig. 6. Here, a fitted sigmoidal curve was utilized and by applying the

Q values corresponding to minimum MSRs converged single curves were successfully obtained.

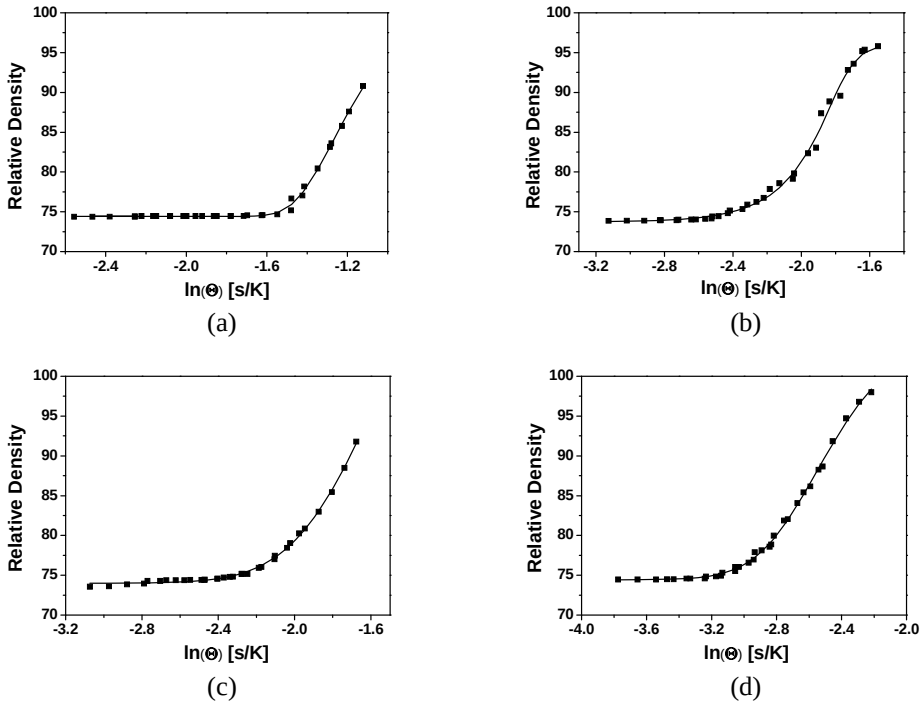


Fig. 6 MSC curve (a) under 20 MPa and (b) 50 MPa for Schedule 1 and (c) under 20 MPa and 50 MPa for schedule 2

2. MSC validation

In order to validate the MSC curve, new densification experiment was performed under 50 MPa with peak temperature at 400℃ with 30 min holding time (the same as in schedule 2) and heating rate of 30℃/min, which was overlapped on MSC shown in Fig. 5 (b). The overlapped MSC is shown in Fig. 6.

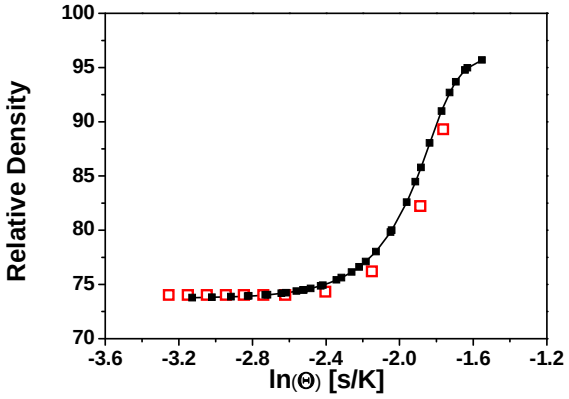


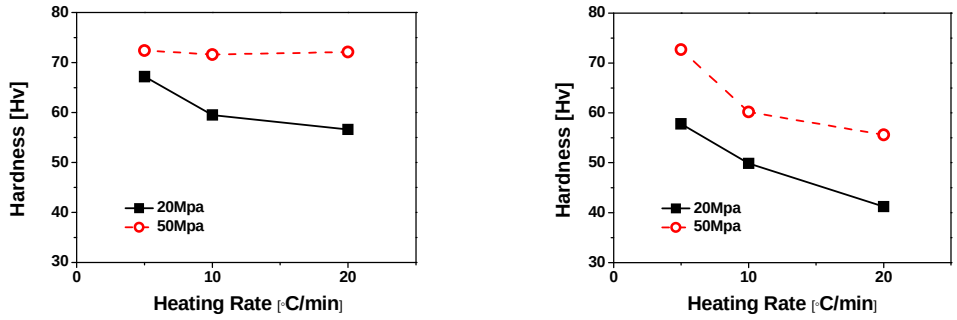
Fig. 6 The overlapped MSC with new data with a heating rate of 30℃/min for Schedule 1

The red empty squares are new set of data with heating rate of 30℃/min and the sigmoidal curve and the dotted squares are the correct fitted MSC and previously compensated data set in terms of lnΘ. As can be seen here, the new data points were well coincident with the MSC curve and the maximum deviation occurs within 2% at the relative density of 83% corresponding to the 10th datum point among new set of data.

From the study of MSC of Al-4%Mg alloy it is realized that a desired relative density associated with desired mechanical properties are expected to be tailored well with the MSC regardless of thermal history at constant pressure by choosing a combination of time and temperature for densification corresponding to a specific target density. Therefore, repeated experimental or manufacturing processing parameter control could be minimized.

3. Mechanical properties

Vickers hardness was measured for each specimen with respect to heating rate. Fig 8 shows the hardness vs. heating rate for (a) schedule 1 and (b) schedule 2.



(a) (b)

Fig. 8 The plot for hardness vs. heating rate for (a) schedule 1 and (b) schedule 2

Hardeness tends to decrease with increasing heating rate for both plots. This trend is stronger in schedule 2, in which peak temperature is 500℃ with no holding time. Sintering is, indeed, densification process by bonding of neighbor particles or grains at certain temperature where mass transport can occur by thermally activated diffusion process. Mass transport is necessarily time consuming process. However, at faster heating rate to reach the desired peak temperature without holding time densification by sintering would not be good enough to provide a material with reasonable strength or hardness because of immature completion of densification. In this respect, 30 min holding time at 400℃ under pressure of 50 MPa, hardness is almost precisely constant over the range of heating rate examined. On the other hand, hardness drops seemingly with increasing heating rate resulting in lack of enough mass transport time. Consequently Hardness and strength is proportional to the degree of densification.

Future Work:

Sintering is a very complex phenomenon that involves diffusional mass transport mechanisms, and is accompanied by the geometric evolution of the powder throughout the whole process. As a result, it is generally not possible to quantitatively predict the sintering behavior of a particular powder specimen even if its thermal history is known. A number of theoretical models had been developed trying to achieve this goal but with little success. However, Master Sintering Curve model greatly simplifies the process and makes final density prediction possible with assumption of only one dominant diffusion mechanism, which can adequately predict sintering results. Rearranging eq. (1) into eq. (2) through a simple variable separation and integration operation by Su and Johnson provided the beauty of MSC in such a way that the left hand side term with all the hard-to-know microstructural parameters can be expressed as the right hand side term with easy-to-know time-temperature parameters acquired from experimental data. The only physical parameter in this equation is apparent activation energy. This value can be found by minimum residual square method or self consistency method although care must be taken to minimize a fluctuation of both initial and final area of densities.

In this respect applying MSC theory to various PM materials not limited to pressurelessly sintered ceramics would provide us with much precious information on internal or microstructural states in a material and allows us to manipulate and make engineering design to attain desirable properties for specific application. Before future work is suggested, several works that have been done is wrapped up to the present.

A. Past work

(1) A sequential combination of PM processes was well developed to fabricate a nanostructured material

(2) These processes were applied to fabricate Al-Mg bulk nano-alloy from powder consolidation to obtain high strength/high formability characteristics in the alloy

(3) The most important parameters, density and grain size, were not easy to control so that we ended up inconsistent results on its mechanical properties. In only 50% out of total number of complete processing cycles we acquired specimens with the desirable properties, which encourage us to develop a unified parametric control process to minimize a deviation in property data.

B. Issue

(1) All the PM scientists and engineers absolutely want to manipulate internal structure determining materials' mechanical/physical characteristics.

(2) To put it concretely it is the best to fabricate PM materials with full density and minimally sustained grain structure.

(3) The goal was approached by repeating experiments or by phenomenological method based on certain theoretical background.

(4) One of the prospective method is to utilize MSC theory in prediction and engineering design of PM material

B. Future work

(1) Applying MSC theory (limited to pressureless sintering) to nano powders of ceramic or metals (would rather focused on pure metal to effect of diffusion by alloy elements each other)
- Selection of material is under consideration now.

(2) Predicting density behavior in terms of time and temperature variables in hot pressing (that is, pressure assisted sintering)
- Of course, as stated in current report, MSC theory developed for pressureless sintering is fairly well applied to pressure-assist sintering as well in our Al-4%Mg consolidation..
- However, currently only low level of pressures (20 and 50 MPa) were applied. It is necessary to check out the validation over the wide range of pressing pressures (low pressure to very high one).

(3) Investigating influence of pressure on sintering to check out if increasing pressure could lower peak temperature corresponding to the maximum shrinkage rate reached.
- This investigation is critically important. If external pressure parameter may be able to lower the sintering temperature, utilizing the very high pressure would make the sintering successful with reducing grain growth behavior due to suppressing thermally activated diffusion process while keeping mass transport mobility still activated under the high pressure circumstance.

(4) Once the studies of (2) and (3) are completed, microstructural evolution during densification should be observed by metallographic method to compare with density variation.

(5) Integrating all the results from (1), (2), and (3) to build up algorithm or system for processing parameter manipulation for the examined material having desired properties.

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